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Sulphur and nitrogen fluxes and budgets in the Bohemian Forest and Tatra Mountains during the Industrial Revolution (1850–2000)

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Abstract

Major fluxes of sulphur and dissolved inorganic nitrogen were estimated in Central European mountain ecosystems of the Bohemian Forest (forest lakes) and Tatra Mountains (alpine lakes) over the industrial period. Sulphur outputs from these ecosystems were comparable to inputs during a period of relatively stable atmospheric deposition ($10\text{--}35\text{ mmol m}^{-2}\text{ yr}^{-1}$) around the 1930s. Atmospheric inputs of sulphur increased by three- to four-fold between the 1950s and 1980s to ~ 140 and $\sim 60\text{ mmol m}^{-2}\text{ yr}^{-1}$ in the Bohemian Forest and Tatra Mountains, respectively. Sulphur outputs were lower than inputs due to accumulation in soils, which was higher in forest soils than in the sparser alpine soils and represented $0.8\text{--}1.6$ and $0.2\text{--}0.3\text{ mol m}^{-2}$, respectively, for the whole 1930–2000 period. In the 1990s, atmospheric inputs of sulphur decreased 80% and 50% in the Bohemian Forest and Tatra Mountains, respectively, and sulphur outputs exceeded inputs. Catchment soils became pronounced sources of sulphur with output fluxes averaging between 15 and $31\text{ mmol m}^{-2}\text{ yr}^{-1}$. Higher sulphur accumulation in the forest soils has delayed (by several decades) recovery of forest lakes from acidification compared to alpine lakes. Estimated deposition of dissolved inorganic nitrogen was $53\text{--}75\text{ mmol m}^{-2}\text{ yr}^{-1}$ in the Bohemian Forest and $35\text{--}45\text{ mmol m}^{-2}\text{ yr}^{-1}$ in the Tatra Mountains in the 1880–1950 period, i.e. below the empirically derived threshold of $\sim 70\text{ mmol m}^{-2}\text{ yr}^{-1}$, above which nitrogen leaching often occurs. Dissolved inorganic nitrogen was efficiently retained in the ecosystems and nitrate export was negligible ($0\text{--}7\text{ mmol m}^{-2}\text{ yr}^{-1}$). By the 1980s, nitrogen deposition increased to ~ 160 and $\sim 80\text{ mmol m}^{-2}\text{ yr}^{-1}$ in the Bohemian Forest and Tatra Mountains, respectively, and nitrogen output increased to 120 and $60\text{ mmol m}^{-2}\text{ yr}^{-1}$. Moreover, assimilation of nitrogen in soils declined from ~ 40 to $10\text{--}20\text{ mmol m}^{-2}\text{ yr}^{-1}$ in the alpine soils and even more in the Bohemian Forest, where one of the catchments has even become a net source of nitrogen. In the 1990s, nitrogen deposition decreased by $\sim 30\%$ and DIN output decreased to <70 and $35\text{ mmol m}^{-2}\text{ yr}^{-1}$ in the Bohemian Forest and Tatra Mountains, respectively. New steady-state conditions, with negligible nitrogen export, could be reached in future but at lower nitrogen depositions than in the 1930s.

Keywords: emission, deposition, acidification, nitrogen-saturation, recovery, sulphate, nitrate, ammonium, mountain lakes

Introduction

Many European and North American regions have recently shown a widespread reversal in surface water acidification due to declining deposition of acidifying compounds (e.g. Stoddard *et al.*, 1999; Evans *et al.*, 2001). The extent and timing of increased acid neutralising capacity (ANC) and pH depends, however, not only on the reduction in emission/deposition rate of sulphur (S) and nitrogen (N) compounds but also on the way that soils and vegetation respond to their reductions (e.g. Wright and Hauhs, 1991; Alewell *et al.*, 2000). Among them, sulphate (SO_4) desorption, organic S cycling in soils (Novák *et al.*, 1996; Torssander and Mörth, 1998; Pechtel *et al.*, 2001) and factors affecting N cycling in catchments (e.g. Dise and Wright, 1995; Aber *et al.*, 1998) are important. Published trends in water chemistry provide

the “only” information on changes in composition relative to changing atmospheric deposition. Studies of element fluxes within the whole ecosystem help to understand the processes contributing to this change.

With the exception of “roof” experiments (e.g. Wright *et al.*, 1993; Hultberg *et al.*, 1998; Gundersen *et al.*, 1998a), the greatest reduction in deposition of acidifying compounds has occurred in Central Europe. This large whole-ecosystem “experiment” has been based on $\sim 80\%$ and $\sim 30\%$ reduction in S and N emissions, respectively, in the area of Germany, Poland, the Czech Republic and Slovakia during the 1990s (Kopáček *et al.*, 2001). Parallel decreases in deposition rates of SO_4 , nitrate (NO_3), and ammonium (NH_4) have resulted in relatively rapid improvement in water quality in acidified

mountain lakes in this area (e.g. Kopáček *et al.*, 1998; Veselý *et al.*, 1998).

In this paper major fluxes of S and N compounds in two Central European mountain areas (Bohemian Forest and Tatra Mountains) are estimated for the whole industrial period. First, historical (1850-2000) emission rates of S and N in the area of the Czech Republic and Slovakia are reconstructed. Second, historical trends in S and N deposition in the mountains are estimated using relationships between emission rate and measured deposition. Third, S and N outputs from catchment-lake ecosystems are estimated using historical and recent water chemistry records. Finally, the input-output fluxes are used to estimate possible changes in soil storage of S and N over the 1930-2000 period.

Methods

SITE DESCRIPTION, WATER AND SOIL CHEMISTRY

The areas of the Bohemian Forest (BF) and Tatra Mountains (TM) are situated at 13°-14° E, 49° N and 20° 10' E, 49° 10' N, respectively. Two lakes (Cerné, CN, and Certovo, CT) were studied in BF (Table 1). These lakes are situated in steep, forested catchments, planted predominantly with Norway spruce and sparse beech. Soils are mostly acidic podzols in different stages of development and/or cambisols (average depth of ~0.6 m) with cation exchange capacity between 16 and 82 eq m⁻² (average of 23 eq m⁻²), base saturation of 10-13% and pH (water extracts; H₂O) of mineral B horizons of 3.7-4.6 (Kopáček, unpubl. data).

Table 1. Major morphological and chemical parameters of the Bohemian Forest (BF) and Tatra Mountains (TM) catchment-lake ecosystems. Chemical composition of lake water refers to September-October 2000 (Kopáček and Stuchlík, unpubl. data). BC, base cations (sum of Ca, Mg, Na and K); DOC and DON, dissolved organic carbon and nitrogen, respectively.

Lake		Cerné	Certovo	Wielki Staw	Morskie Oko	Vyšné Wahlenbergovo
Code		CN	CT	WS	MO	VW
Location		BF	BF	TM	TM	TM
Max. depth	m	40	36	79.3	50.8	20
Area	ha	18.4	10.3	34.4	34.9	5.2
Volume	10 ³ m ³	2880	1850	12970	9940	421
Catchment	ha	129	86	493	653	32
Min. altitude	m a.s.l.	1008	1028	1665	1395	2145
Max. altitude	m a.s.l.	1343	1343	2300	2499	2405
Soils ¹⁾	kg m ⁻²	165	240	82	66	20
Vegetation	in % of area	90-forest	90-forest	45-meadows	20-meadows	11-meadows
		(Norway spruce)	(Norway spruce)	15-dwarf pine	30-dwarf pine	46-moraine
				25-moraine	and/or forest	43-bare rocks
				15-bare rocks	15-moraine	
					40-bare rocks	
pH		4.9	4.6	6.7	6.9	6.3
HCO ₃ ⁻	µeq l ⁻¹	0	0	73	130	29
SO ₄ ²⁻	µeq l ⁻¹	87	91	44	56	31
NO ₃ ⁻	µeq l ⁻¹	62	35	19	24	26
Cl ⁻	µeq l ⁻¹	19	18	3	4	5
NH ₄ ⁺	µeq l ⁻¹	1	2	1	1	1
BC	µeq l ⁻¹	141	85	145	217	95
Al _i ⁿ⁺	µeq l ⁻¹	20	33	<0.5	<0.5	<0.5
DOC	µmol l ⁻¹	83	233	34	39	13
DON	µmol l ⁻¹	9	13	7	6	5

¹⁾ Average bulk density of soil (<2 mm, 105 °C dried), calculated as area weighted mean including moraine and bare rocks (Kopáček, unpubl. data).

Bedrock is formed primarily of mica-schists (muscovitic gneiss), with small quartzite intrusions (Veselý, 1994).

Despite their relatively rapid reversal from acidification and N saturation (Kopáček *et al.*, 1998; Veselý *et al.*, 1998), both lakes are still acidic, with elevated concentrations of aluminium (Al) (Table 1). Trends in concentrations of SO_4 , NO_3 , and NH_4 in CN and CT come from Jírovec and Jírovcová (1937), Veselý *et al.* (1998), Procházková and Blažka (1999), and Stuchlík and Kopáček (unpubl. data). The historical data used before 1984 has been found to be reasonably reliable (Veselý and Majer, 1992; Procházková and Blažka, 1999). Background (pre-acidification) concentrations of SO_4 in CN and CT have been estimated to be ~ 16 and $\sim 20 \mu\text{mol l}^{-1}$, respectively, by Veselý and Majer (1992).

Three lakes (Wielki Staw, WS; Morskie Oko, MO, and Vyšné Wahlenbergovo, VW) were studied in TM. WS and VW are situated in the alpine zone, while MO is below the local tree line with $>80\%$ of catchment in the alpine zone. Dry alpine meadows and sparse dwarf pine represent the dominant vegetation in these catchments (Table 1). Bedrock is mostly composed of granodiorite. Soils above the tree line are undeveloped alpine soils (lithosol, ranker) with average depth of ~ 0.5 m, mean cation exchange capacity of 12 eq m^{-2} , base saturation of 11%, and pH (H_2O) of mineral horizons of 4.7 (Kopáček, unpubl. data). The carbonate buffering system of WS and MO was not depleted during acidification and has been recently recovered in VW (Kopáček *et al.*, 1998). Trends in concentrations of SO_4 and NO_3 in WS, MO, and VW come from Stangenberg (1938), Bombówna, (1965), Henriksen *et al.* (1992), Bombówna and Wojtan (1996), and Kopáček and Stuchlík (1994 and unpubl. data).

Concentrations of dissolved organic nitrogen (DON) in BF and TM precipitation and total DON in lakes were determined over the 1997–2000 and 1986–2000 period, respectively, by Kjeldahl combustion according to Procházková (1960). Concentrations of organic carbon (C) and total N in soil samples were analysed by CN analyser (NC 2100, ThermoQuest, Italy). Total S was determined after mineralisation and precipitation as BaSO_4 , and water extractable SO_4 -S was determined according to Alewell (1998). Average areal amount of these elements (mol m^{-2}) was calculated from their average contents in soil (mol kg^{-1}) and bulk density of soil (kg m^{-2}). In TM catchments with large areas of bare rock and moraine, the average areal amounts of elements were calculated as area weighted means. These hypothetical values represent a situation where soils were uniformly distributed over the whole catchment (Table 1). Average bulk densities of soil used in this calculation were 122 and 33 kg m^{-2} for alpine meadows and moraine, respectively (Kopáček, unpubl. data).

EMISSION AND DEPOSITION RATES OF SULPHUR AND NITROGEN

The historical Czech and Slovak (CS) and Central European (Germany, Poland, Czech Republic, and Slovakia) emission trends for sulphur dioxide (SO_2), nitrogen oxides (NO_x), and ammonia (NH_3) were obtained similarly to Kopáček *et al.* (1998) but for a longer period. Details are given in Appendix 1.

Long-term trends in throughfall and bulk deposition of SO_4 , NH_4 and NO_3 in the BF and TM were estimated using their relationships with long-term trends in deposition of S and N compounds in the Czech Republic and northern Slovakia (Chopok). These estimations were based on ratios between the measured depositions in BF and wet-only deposition in the Czech Republic, and on ratios between the measured bulk depositions in TM and bulk depositions in northern Slovakia (Appendix 2). Long-term trends in deposition of SO_4 , NH_4 , and NO_3 were estimated from relationships between measured deposition and the respective CS emissions of SO_2 , NH_3 and NO_x . Details on data sources, calculation, significance of relationships and uncertainty are given in Appendix 2.

SULPHUR AND NITROGEN FLUXES

Mass balance of S and N in catchment-lake ecosystems was estimated using Eqn. (1):

$$M_{\text{OUTPUT}} = M_{\text{INPUT}} - R_{\text{SOIL}} - R_{\text{LAKE}} - \Delta M_{\text{LAKE}} \quad (1)$$

where M_{INPUT} and M_{OUTPUT} are S or N input and output to/from the catchment-lake ecosystem, respectively. R_{SOIL} and R_{LAKE} are net mass retention (or production when negative) of S or N in the soil and lake, respectively. ΔM_{LAKE} is the change in storage of S or N in the lake and was obtained as the difference between its amount at the end and beginning of the mass budget period.

Atmospheric deposition was assumed to represent the dominant part of M_{INPUT} for both S and N. In this simplified approach S input from weathering was neglected. Similarly, assimilation of atmospheric N by terrestrial vegetation and N losses due to denitrification were assumed to be negligible in comparison to other N fluxes (Williams *et al.*, 1995; Gundersen *et al.*, 1998a) and to be roughly equal (Curtis *et al.*, 1998). Sulphur input was calculated from estimated trends in throughfall and bulk deposition to the respective areas of forest and bare surface (including lake) in BF, and from estimated trend in bulk deposition of S in TM. Dry deposition of S in TM was only $\sim 10\%$ of total S deposition in 1996 (Lydersen *et al.*, 1997) and was neglected. Input of N was the sum of estimated deposition of dissolved inorganic

nitrogen ($\text{DIN} = \text{NO}_3\text{-N} + \text{NH}_4\text{-N}$; in throughfall and/or bulk) and bulk deposition of DON. The average bulk deposition of DON in the 1997-2000 period (13 and 7 $\text{mmol m}^{-2} \text{yr}^{-1}$ in BF and TM, respectively) was used for a rough estimation of DON deposition over the 1930-2000 period assuming no important trend (Kopáček *et al.*, 1997).

M_{OUTPUT} of S and DIN from catchment-lake ecosystems were calculated from the measured concentrations of SO_4 , NO_3 and NH_4 in the lakes and the average annual water output. Mass balance over the 1930-2000 period was estimated assuming a linear trend between the measured data. The average lake water concentrations of total DON for the last decade were used to estimate cumulative DON flux from lakes over the whole 1930-2000 period, assuming negligible historical changes in DON concentrations in these phosphorus-limited water bodies (Kopáček *et al.*, 1995).

The average annual water output from BF catchment-lake ecosystems was assumed to be $1.2 \text{ m}^3 \text{m}^{-2} \text{yr}^{-1}$ and constant for the 1930-2000 period. This value was based on the average throughfall deposition to the lakes (1387 mm over the 1991-2000 period), 15% evaporation of throughfall (Kopáček *et al.*, 2000a), and long-term (1961-2000) precipitation in BF. For TM lakes, the specific outflow was 1.42 and $1.57 \text{ m}^3 \text{m}^{-2} \text{yr}^{-1}$ for the south (VW) and north (WS and MO) part of the mountains (Lajczak, 1996). Uncertainty associated with S or N output from ecosystems in individual years was roughly estimated as a coefficient of variation of the average level of precipitation ($\pm 15\%$ for BF).

In-lake retention of SO_4 and NO_3 was calculated according to Kelly *et al.* (1987), when the original relationship between in-lake reduction in SO_4 or NO_3 concentrations and their loading was rearranged into the form:

$$R_{\text{LAKE}} = LA \left(1 + \frac{Q}{AS_M}\right)^{-1} \quad (2)$$

where L is areal SO_4 or NO_3 loading (terrestrial output and deposition to lake; $\text{mol m}^{-2} \text{yr}^{-1}$), A is lake area (m^2), Q discharge ($\text{m}^3 \text{yr}^{-1}$), and S_M is mass transfer coefficient. S_M was set here to the values 0.4 and 7.4 m yr^{-1} for SO_4 and NO_3 , respectively (Kelly *et al.*, 1987). A lower S_M (5 m yr^{-1}) was used for NO_3 in colder alpine lakes in TM (Curtis *et al.*, 1998). Finally, R_{SOIL} was calculated by difference from Eqn. (1).

Major fluxes of S and N calculated from Eqns. (1) and (2) were compared to measured fluxes within CT catchment-lake ecosystem. This mass budget was based on regular sampling of throughfall, precipitation, all surface tributaries and outflow (calibrated weir) in two-week to four-week intervals during the 1998-2000 period (Kopáček *et al.*, 2000a).

Results and discussion

SULPHUR

Trends in emission and deposition rates of sulphur

Emission rate of SO_2 increased nearly linearly between 1850 and 1950 (from ~ 18 to $\sim 100 \text{ mmol m}^{-2} \text{yr}^{-1}$, respectively) in the area of the Czech Republic and Slovakia (Fig. 1A). Heavy industrial production in this area after World War II resulted in a sharp increase in energy consumption, primarily based on lignite combustion, and consequently in an extremely high annual increase in SO_2 emissions ($\sim 10 \text{ mmol m}^{-2} \text{yr}^{-1}$). Emissions of SO_2 increased four-fold between 1950 and the middle 1980s, levelled off at $390 \text{ mmol m}^{-2} \text{yr}^{-1}$ in the first half of the 1980s, and then decreased sharply ($\sim 21 \text{ mmol m}^{-2} \text{yr}^{-1}$) in the 1985-1999 period (Fig. 1A). In 1999, CS emissions of SO_2 were similar to those in the 1930s. Large reduction in lignite combustion and sulphur emission controls were the primary reasons for these recent changes (Kopáček *et al.*, 1997, 1998).

The long term trend in CS emissions of SO_2 is similar to the Central European trend, except for the 1970s and 1980s (Fig. 1A), when CS emissions of SO_2 increased more sharply, due to extremely high emission rates in the German-Polish-Czech border area with numerous electric power plants, to a maximum SO_2 emissions of $\sim 800 \text{ mmol m}^{-2} \text{yr}^{-1}$. Consequently, the decrease in SO_2 emissions was more pronounced in CS ($\sim 85\%$) than the Central European trend ($\sim 70\%$).

Deposition rates of S in the Czech Republic and northern Slovakia, which were estimated from the trend in CS emissions of SO_2 , are given in Fig. 1B. The estimated deposition agrees well ($P < 0.001$) with measured deposition. Trends in estimated S deposition in BF and TM are given in Figs. 1C and 1D, respectively. Deposition was relatively stable in both areas in the first half of the 20th century, rapidly increased between 1950 and 1980, and reached a maximum in the early 1980s. Estimated deposition maxima were ~ 165 and $\sim 50 \text{ mmol m}^{-2} \text{yr}^{-1}$ in BF (throughfall and bulk deposition, respectively) and $\sim 60 \text{ mmol m}^{-2} \text{yr}^{-1}$ in TM. Recent S deposition has been $\sim 80\%$ lower than in the 1980s in BF, being similar to the 1930s, and $\sim 50\%$ lower in TM, approaching levels from the late 1950s (Figs. 1C and D).

Fluxes and mass budget of sulphur

Comparison between S fluxes estimated from Eqns. (1) and (2) and measured by mass budget studies (Kopáček *et al.*, 2000a; and unpubl. data) are given for CT catchment-lake ecosystem in Table 2. There are only small differences between the results primarily due to different precipitation

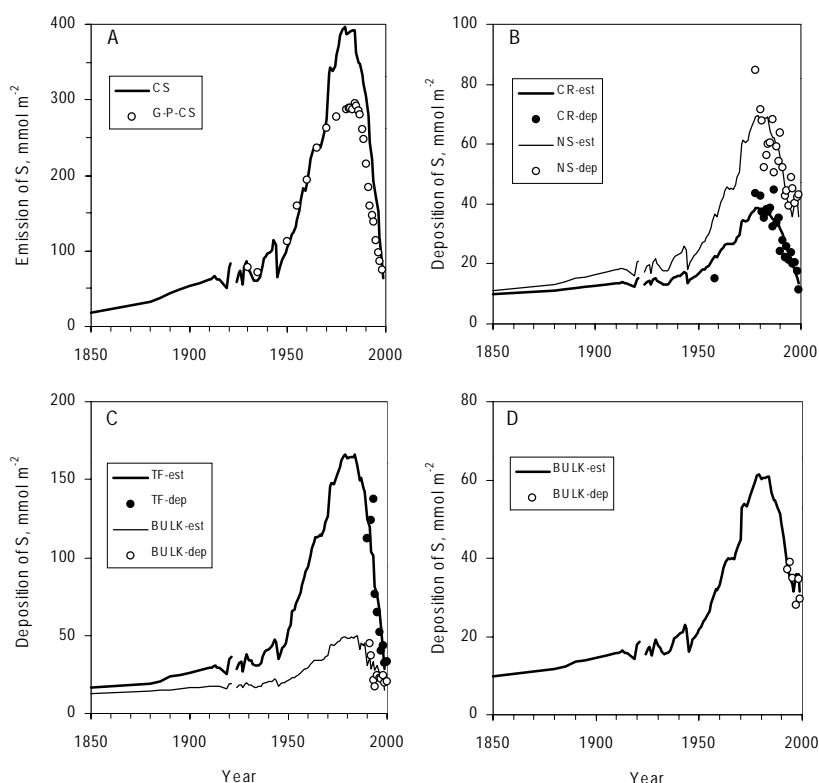


Fig. 1. Trends in emission and deposition rate of S: (A) Emissions of SO_2 in the area of the Czech Republic and Slovakia (CS) and in Central Europe (Germany, Poland, Czech Republic and Slovakia, G-P-CS; Mylona, 1993; Berge, 1997). (B) Comparison between estimated and measured wet-only and bulk deposition of $\text{SO}_4\text{-S}$ in the Czech Republic (CR) and northern Slovakia (NS), respectively. (C) Comparison between estimated and measured throughfall (TF) and bulk (BULK) deposition of $\text{SO}_4\text{-S}$ in the Bohemian Forest. (D) Comparison between estimated and measured bulk (BULK) depositions of $\text{SO}_4\text{-S}$ in the Tatra Mountains. All data are based on annual means.

Table 2. Comparison between S fluxes in the Certovo catchment-lake ecosystem (CT), estimated from Eqns. (1) and (2) and measured (Kopáček *et al.* 2000a; and unpubl. data). Data are averages for 1998–2000 period; units are kmol yr^{-1} .

	estimated	measured
M_{INPUT}	29.1	31.4
M_{OUTPUT}	56.3	61.8
ΔM_{LAKE}	N*	-3.5
R_{LAKE}	1.9	4.3
R_{SOIL}	29.1	31.3

*N, neglected

levels (long-term average *vs.* real data) and the neglected change in S storage in the lake (dilution) in the more simple approach. Estimated data based on only sparse observations thus provide a reasonable estimation of the real S fluxes.

The upper part of Fig. 2 shows trends in estimated input

and output fluxes of S in BF and TM catchment-lake ecosystems, while the lower part shows historical changes in ratios of S-output to S-input ($S_{\text{out}} : S_{\text{in}}$). Sulphur input exceeded S output only slightly in the 1930s in both mountain areas and $S_{\text{out}} : S_{\text{in}}$ ratios were between 0.5 and 1 (Figs. 2C and D). This suggests low accumulation of S in soils and more or less steady state conditions. Under increasing S atmospheric input, however, the soil in both areas started to accumulate more S. Even in the early 1980s, $S_{\text{out}} : S_{\text{in}}$ ratios were < 1 despite the highest deposition rate of S. There were only small changes in the rate of S retention in forest soils between the 1960s and 1980s and they still continued to accumulate S (Fig. 2C). In contrast, alpine ecosystems of TM with thinner soil cover showed more pronounced signs of S-saturation (higher $S_{\text{out}} : S_{\text{in}}$ ratios), and after the decline in S deposition rate, $S_{\text{out}} : S_{\text{in}}$ ratios increased to > 1 indicating that alpine ecosystems have become a source of S (Fig. 2D).

While both BF lakes, with comparable terrestrial characteristics and relatively abundant soils, have responded nearly uniformly and $S_{\text{out}} : S_{\text{in}}$ ratios remained high in the 1990s (Fig. 2C), responses of alpine TM lakes differed

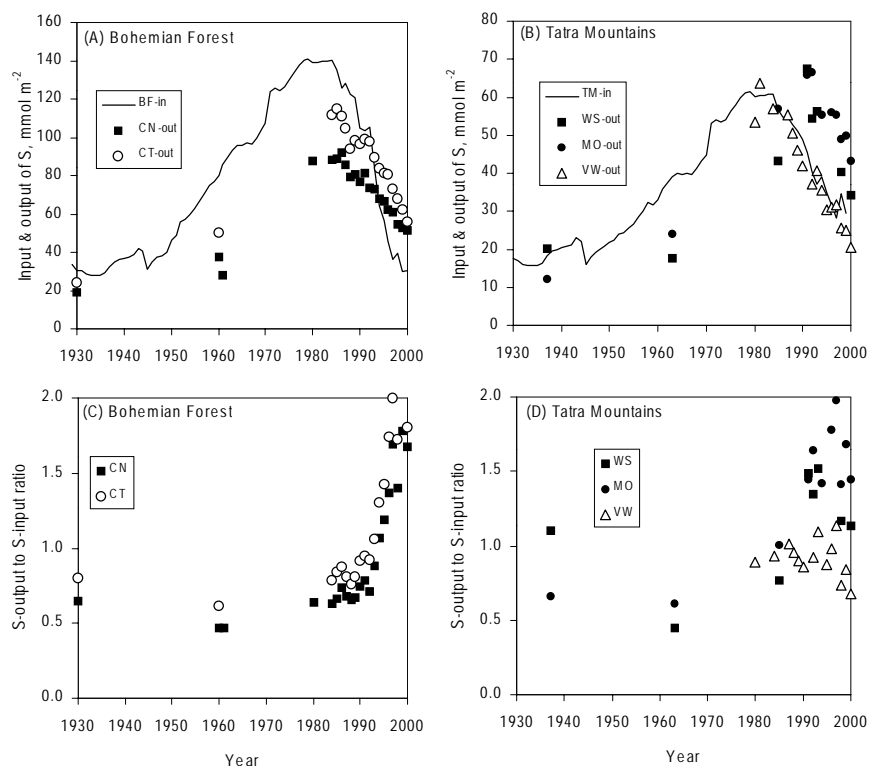


Fig. 2. Trends in S fluxes. Upper part: Comparison of S-input by atmospheric deposition in the Bohemian Forest (A) and Tatra Mountains (B) to the S-output from catchment-lake ecosystems in the 1930-2000 period. Data on S output from CN and CT in 1930 are based on estimated background concentrations of SO_4 in the lakes (Veselý and Majer, 1992). Lower part (C,D): Ratio of S-output to S-input. For lake codes see Table 1. All data are based on annual means.

according to the amount of soil (Figs. 2B and 2D). The smallest amount of soil is in the VW catchment where the low S retention capacity has resulted in relatively small changes in $S_{\text{out}} : S_{\text{in}}$ ratio (around 1) throughout the 1980-2000 period. Catchments of WS and MO lakes are covered with alpine meadows and have higher S retention capacity. Consequently, $S_{\text{out}} : S_{\text{in}}$ ratios increased to >1 , reached their maxima in 1997 and have been decreasing since. This suggests that new steady state conditions in the soil S pool of alpine ecosystems can be reached relatively rapidly after reduction of S deposition, while this process may last substantially longer in forest ecosystems with deeper soils (e.g. Torssander and Mörtz, 1998; Prechtel *et al.*, 2001).

Cumulative atmospheric input of S over the whole period of the Industrial Revolution (1850–2000) was estimated to be 7.2 mol m^{-2} in BF and 3.5 mol m^{-2} in TM. Most of this S (70–80%) was deposited in the 1930–2000 period (Table 3). Differences in S loading between the mountain areas were due mainly to differences in vegetation cover (trees vs. meadows). The forested area of BF had a higher specific surface area and, consequently, higher dry and occult deposition of S (throughfall and bulk deposition in Fig. 1C).

Cumulative S output from the forest sites was 67–82% of S deposition over the 1930–2000 period compared with S

accumulation in soils of 15–29% (Table 3). Lower cumulative output and higher accumulation of S in soils was observed in CN catchment and resulted in higher total S in the soil (Table 3). The difference between S concentration in BF soils in the year 2000 and S accumulation over the 1930–2000 period was used to assess soil S content in the 1930s, i.e. during equilibrium between S input and output. These estimated steady-state pools of S in BF soils were similar in both CT and CN catchments ($1.6\text{--}1.8 \text{ mol m}^{-2}$).

The Bohemian Forest soils became a net source of $\text{SO}_4\text{-S}$ around 1993–1994 (Fig. 2), similar to the most damaged Central European region (the Ore Mountains; Novák *et al.*, 2000) but were one order of magnitude lower. The average annual $\text{SO}_4\text{-S}$ leaching from CN and CT soils was 19 and $31 \text{ mmol m}^{-2} \text{ yr}^{-1}$, respectively, over the 1994–2000 period. Based on the amount of water extractable $\text{SO}_4\text{-S}$ in BF soils in 2000 (Table 3), it is estimated that a similar level of leaching would only continue for the next five years. The soil $\text{SO}_4\text{-S}$ pool, however, is also supplied by mineralisation of organic S (Novák *et al.*, 1996; Torssander and Mörtz, 1998), as well as from sources of inorganic S (e.g. Al-SO_4 complexes; Nordstrom, 1982). Therefore, if all of the S accumulated in BF soils over the 1930–2000 period was

Table 3. Cumulative S budgets in the Bohemian Forest (CN and CT) and Tatra (WS and MO) catchment-lake ecosystems. Numbers in brackets represent relevant year and/or period. For lake codes see Table 1. All units are mol m⁻². ND, not determined.

	<i>CN</i>	<i>CT</i>	<i>WS</i>	<i>MO</i>
Cumulative S deposition (1850-2000)	7.1	7.2	3.5	3.5
Cumulative S deposition (1930-2000)	5.5	5.6	2.6	2.6
Cumulative S output (1930-2000)	3.7	4.6	2.3	2.3
In-lake retention of S (1930-2000) ¹⁾	0.17	0.17	0.04	0.03
Change in S content in lake water (1930-2000) ¹⁾	0.06	0.06	0.02	0.03
S retention in soil (1930-2000)	1.6	0.8	0.3	0.2
Total S content in soil (2000)	3.3	2.6	1.2	1.0
Water extractable SO ₄ -S in soil (2000)	0.101	0.117	0.014	0.011
Estimated total S content in soil (1930) ²⁾	1.6	1.8	0.9	0.8

¹⁾In-lake SO₄ reduction and change in SO₄ content in lake water (mol) were recalculated per total catchment area (mol m⁻²).

²⁾Estimated total S content in soil in 1930 was the difference between the total S content in soil in 2000 and the estimated S retention in soil over the 1930-2000 period.

available and could be transported at the present leaching rate, the process of S wash out would last about 26 years for CT and 84 years for CN. Part of the organically-bound S, however, may be volatilised after its mineralisation by soil micro-organisms (Novák *et al.*, 2000), which would reduce the time of S wash out. On the other hand, the S leaching rate may gradually decrease and S removal may last longer.

The thinner soil cover in alpine catchments (TM soils) accumulated smaller amounts of S compared to the forest sites in BF. Sulphur accumulation in TM soils represented only ~10% of S deposited over the 1930-2000 period, while ~90% of this load was leached (Table 3). TM soils had already become a net source of SO₄-S in the late 1980s with an average annual SO₄-S leaching of 15 and 21 mmol m⁻² yr⁻¹ (at WS and MO, respectively). The pool of water extractable SO₄-S in TM soils was one order of magnitude lower than in BF soils (Table 3) and equalled approximately the average annual leaching of SO₄-S from TM soils. Assuming S leaching from the total pool of S, which accumulated in the soil over the 1930–2000 period, the time for S wash out is estimated as 10 years for MO and 20 years for WS at the present S deposition rate. The process of total wash out of anthropogenic S, however, will probably last substantially longer in TM because SO₄-S leaching decreased over the last decade, being 15–27 mmol m⁻² yr⁻¹ in 1991–1992 and 5–14 mmol m⁻² yr⁻¹ in 2000 (Fig. 2D).

NITROGEN

Trends in emission and deposition rates of oxidised nitrogen forms

The emission rate of NO_x increased relatively slowly between 1850 and 1950 (from 10 to 55 mmol m⁻² yr⁻¹) and then by ~4 mmol m⁻² yr⁻¹ up to around 190 mmol m⁻² yr⁻¹ in the 1980s (Fig. 3A). Since 1989, NO_x emissions have decreased primarily due to optimisation of combustion regimes at the main stationary sources. The decrease in NO_x emissions was rapid (~17 mmol m⁻² yr⁻¹) up to 1994, then less pronounced and by 1999 emissions were 88 mmol m⁻² yr⁻¹. Available data on Central European emissions of NO_x were similar to the CS emission trend (Fig. 3A).

Estimated long-term trends in wet-only and bulk deposition of NO₃ in the Czech Republic and northern Slovakia (Fig. 3B) agree well with the measured data (wet-only, P<0.001; bulk, P<0.05) and provide a reasonable background for estimation of throughfall and bulk deposition of NO₃ in BF and TM (Figs. 3C and 3D). According to this estimation, NO₃ deposition rapidly increased in both mountain areas between 1950 and 1980 and reached their maxima of ~100 and ~35 mmol m⁻² yr⁻¹ (throughfall in BF and bulk in TM, respectively) in the late 1980s. During the 1990s, NO₃ deposition has decreased by 30-35% and 1999 levels are comparable to the middle 1960s.

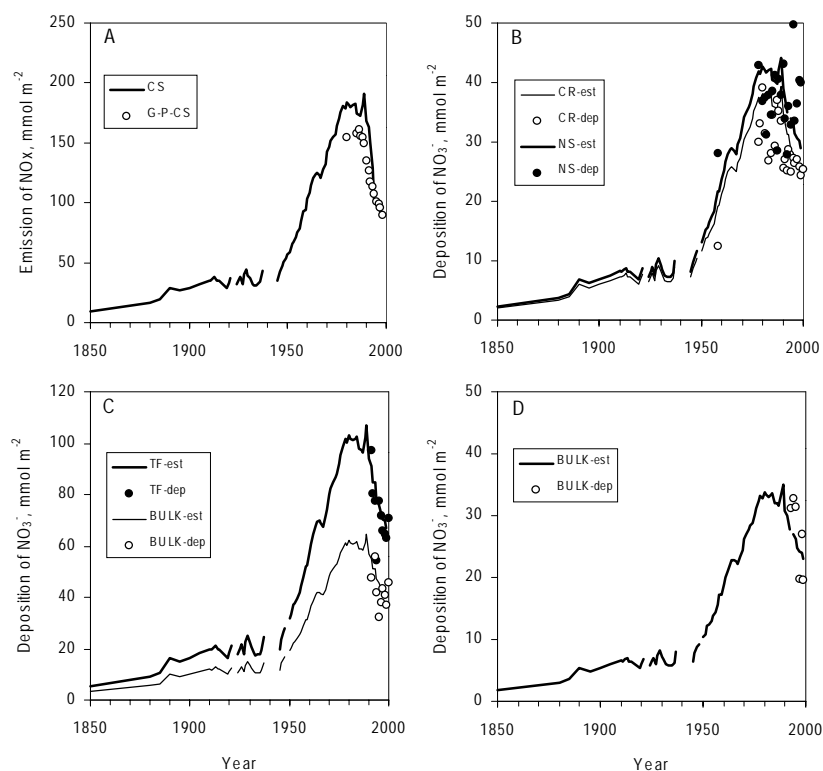


Fig. 3. Trends in emission and deposition rate of oxidised N forms: (A) Emissions of NO_x in the area of the Czech Republic and Slovakia (CS) and in Central Europe (Germany, Poland, Czech Republic and Slovakia, G-P-CS; Berge, 1997). (B) Comparison between estimated and measured wet-only and bulk deposition of $\text{NO}_3\text{-N}$ in the Czech Republic (CR) and northern Slovakia (NS), respectively. (C) Comparison between estimated and measured throughfall (TF) and bulk (BULK) deposition of $\text{NO}_3\text{-N}$ in the Bohemian Forest. (D) Comparison between estimated and measured bulk deposition of $\text{NO}_3\text{-N}$ in the Tatra Mountains. All data are based on annual basis.

Trends in emission and deposition rates of reduced nitrogen forms

The trend in emission rate of NH_3 followed a different pattern to SO_2 and NO_x emissions (Fig. 4A) being mostly derived from agricultural production. CS emissions of NH_3 were on average 25% lower than Central European emissions primarily due to the high emission rate of NH_3 in Germany (Berge, 1997). Cattle and pig production contributed around 65% to 85% to the total anthropogenic CS emissions of NH_3 over the whole 1850–2000 period. The emission rate of NH_3 was already high ($\sim 40 \text{ mmol m}^{-2} \text{ yr}^{-1}$) in 1850, increased only slightly between 1850 and 1920 due to increasing number of inhabitants, and was relatively stable in the 1920–1950 period ($\sim 55 \text{ mmol m}^{-2} \text{ yr}^{-1}$). Between 1950 and 1980, NH_3 emissions increased by $\sim 1 \text{ mmol m}^{-2} \text{ yr}^{-1}$ and levelled off at $88 \text{ mmol m}^{-2} \text{ yr}^{-1}$ in the 1980s (Fig. 4A). Then, NH_3 emissions decreased primarily due to a 55% reduction in cattle production and fertilisation of farmland. As with NO_3 , this decrease was more rapid in the 1990–1994 period than in the second half of the 1990s. In 1999, CS emissions of NH_3 were comparable to the situation one century ago (Fig. 4A).

Estimated long-term trends in wet-only and bulk deposition of NH_4 in the Czech Republic and northern Slovakia agree well ($P < 0.001$) with the measured data (Fig. 4B) and provide a reasonable background for estimation of throughfall and bulk deposition of NH_4 in BF and TM. According to this estimation (Figs. 4C and 4D), NH_4 deposition was relatively stable in both mountain areas between 1850 and 1950, being $34\text{--}45 \text{ mmol m}^{-2} \text{ yr}^{-1}$ in BF throughfall and $26\text{--}36 \text{ mmol m}^{-2} \text{ yr}^{-1}$ in TM bulk deposition. Then, NH_4 deposition increased by $\sim 15 \text{ mmol m}^{-2}$ in both mountain areas between 1950 and 1980, stabilised in the 1980s and decreased 25–27% during the 1990s. Consequently, present NH_4 deposition is comparable with levels in the 1900–1950 period in both areas (Figs. 4C and 4D).

Fluxes and mass budget of nitrogen

Trends in the atmospheric input of DIN and its output from catchment-lake ecosystems of BF and TM are shown in the upper part of Fig. 5. In both areas, DIN outputs were close to zero in the 1930s, increased in parallel with DIN

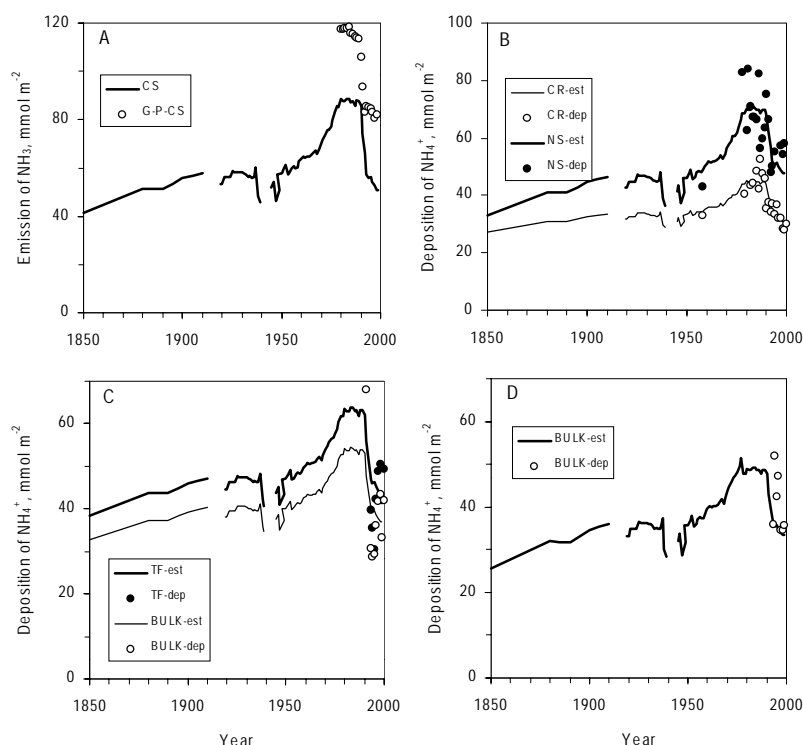


Fig. 4. Trends in emission and deposition rate of reduced N forms: (A) Emissions of NH_3 in the area of the Czech Republic and Slovakia (CS) and in Central Europe (Germany, Poland, Czech Republic and Slovakia, G-P-CS; Berge, 1997). (B) Comparison between estimated and measured wet-only and bulk deposition of $\text{NH}_4\text{-N}$ in the Czech Republic (CR) and northern Slovakia (NS), respectively. (C) Comparison between estimated and measured throughfall (TF) and bulk (BULK) deposition of $\text{NH}_4\text{-N}$ in the Bohemian Forest. (D) Comparison between estimated and measured bulk deposition of $\text{NH}_4\text{-N}$ in the Tatra Mountains. All data are based on annual means.

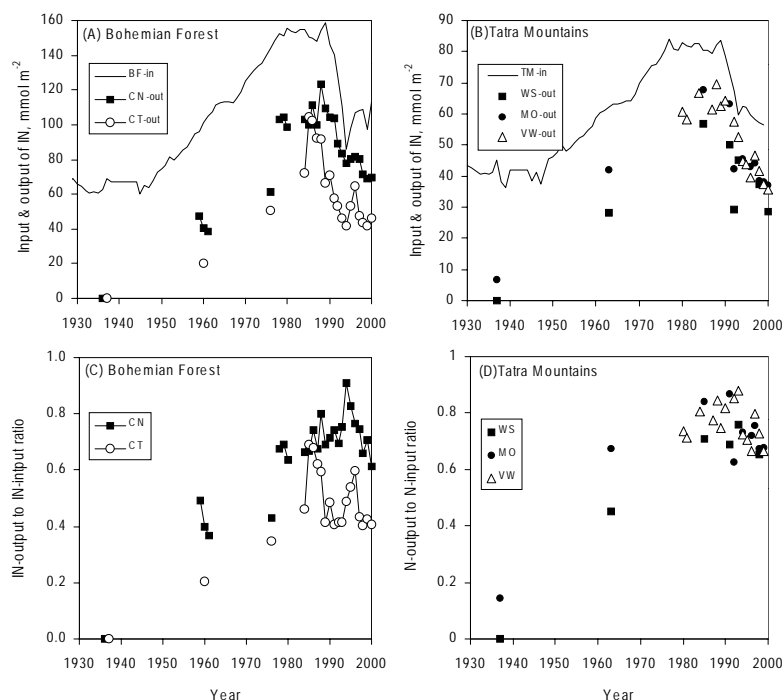


Fig. 5. Trends in fluxes of dissolved inorganic nitrogen ($\text{DIN} = \text{NH}_4\text{-N} + \text{NO}_3\text{-N}$). Upper part: Comparison of DIN input by atmospheric deposition in the Bohemian Forest (A) and Tatra Mountains (B) to the DIN output from catchment-lake ecosystems in the 1930–2000 period. Lower part (C, D): Ratio of DIN output to DIN input. For lake codes see Table 1. All data are based on annual basis.

deposition during the next four decades and reached a plateau in the 1980s. During the last decade, DIN outputs have decreased from all lakes. In contrast to S, ratios of N-output to N-input ($N_{out}:N_{in}$) paralleled the increase and decrease in deposition rate and did not exceed 1 in any lake after the deposition decline (lower part of Fig. 5). The estimated DIN fluxes reasonably reflect these trends, although the magnitude of the values is uncertain for two major reasons.

First, total deposition of DIN was probably higher than the estimated throughfall and bulk deposition given in Figs. 3-5. Throughfall DIN includes N derived from wet plus dry and cloud deposition less net N removal by canopy assimilation (e.g. Dise *et al.*, 1998). The later process modifies significantly the composition of atmospheric deposition (Lovett, 1992). The average ratio between throughfall and bulk deposition of DIN was 1.3 in BF. Lovett (1992) has shown that total atmospheric deposition of DIN into forest sites generally exceeds bulk deposition by a factor of 1.2-1.9. Using the upper factor of 1.9 for BF (due to being in the vicinity of large NO_x emissions sources), the estimated throughfall deposition of DIN into this area was 35–40% underestimated. Similarly, in TM, dry deposition was probably an important source of DIN. Lydersen *et al.* (1997) estimated dry deposition of oxidised and reduced N forms to be 7 and 12 $mmol\ m^{-2}\ yr^{-1}$ in 1996 in TM, which represented 25% of total DIN deposition.

Second, comparison between estimated fluxes and measured fluxes at CT provides evidence that DIN output from catchment-lake ecosystems was underestimated (Table 4). The 1998–2000 average output of DIN from CT was 35% higher than the estimated flux. This is due to the seasonality in NO_3 concentrations in the lake outflow with minima during the vegetation growing season and maxima

in late winter. Historical NO_3 concentrations on BF and TM lakes used in this study were mostly based on summer or early autumn observations and were lower than volume weighted mean concentrations. For example, in CT and CN lakes, volume weighted mean concentrations of NO_3 were 12–44% higher than autumn concentrations in the 1998–2000 period (e.g. in 2000, 56 v. 39 $\mu mol\ l^{-1}$ in CT and 64 v. 57 $\mu mol\ l^{-1}$ in CN). Consequently, the 30–40% underestimation of DIN deposition was in part compensated by a similar underestimation of DIN output from the ecosystem which reduced the error in estimation of long-term retention of DIN in the soils.

In-lake retention of DIN was a significant component of N fluxes within the catchment-lake ecosystems. There was a good agreement between estimated and measured in-lake DIN retention for both CT (Table 4) and CN (42 and 53 $kmol\ yr^{-1}$, respectively). Another approach to estimating in-lake retention of DIN was used based on the accumulation rate of N in sediments. Veselý *et al.* (1993) estimated a mass accumulation rate of 53 $g\ m^{-2}\ yr^{-1}$ in CT over the last century, while the average N content of the uppermost (1-cm) layer was 2.4 $mmol\ g^{-1}$ (Kopáček, unpubl. data) and the resulting N retention in sediments was 13 $kmol\ yr^{-1}$. This estimate is in concordance with measured in-lake retention of DIN (Table 4), although somewhat lower because the measured in-lake N retention also includes N losses due to denitrification.

The cumulative atmospheric inputs of DIN in the 1930–2000 period surprisingly represented “only” ~60% of cumulative DIN deposition from 1850 to 2000 (Table 5). The primary reason was high NH_4 deposition throughout the whole period (Fig. 4). Between 30% to 60% of DIN inputs were leached from the catchments and 10–20% were removed by in-lake processes. Cumulative outputs of DON were higher than inputs and represented an important proportion (26–38%) of total N export from ecosystems (Table 5). The net N retention in BF soils based on Eqn. (1) was 20% and 40% of the N input (DIN plus DON) in CN and CT catchments, respectively, while the N budget for TM lakes indicates a similar relative retention (35% and 20%) of N in alpine soils but at lower absolute values (Table 5).

The N concentrations of BF and TM soils in 2000 was more than an order of magnitude higher than N retention in soils over the 1930–2000 period (Table 5). Ratios of C:N averaged 22 and 24 in forest catchments and 18 in alpine catchments. At soil C:N ratios of 25 or less, there is a potential risk of elevated export of DIN from soils (Gundersen *et al.*, 1998b). Hypothetical soil C : N ratios in the 1930s, estimated from the present soil composition, were slightly higher but already ≤ 25 (Table 5). A relatively low

Table 4. Comparison between DIN fluxes in the Certovo catchment-lake ecosystem (CT), estimated from Eqns. (1 and 2) and measured (Kopáček *et al.* 2000a; and unpubl. data). Data are averages for 1998-2000 period; units are $kmol\ yr^{-1}$

	<i>estimated</i>	<i>measured</i>
M_{INPUT}	93.3	97.8
M_{OUTPUT}	40.3	62.7
ΔM_{LAKE}	N*	-0.3
R_{LAKE}	18.6	22.8
R_{SOIL}	34.4	12.7

*N, neglected

Table 5. Cumulative budgets of N in the Bohemian Forest (CN and CT) and Tatra (WS and MO) catchment-lake ecosystems. Numbers in brackets represent relevant year and/or period. For lake codes see Table 1. All units are mol m⁻² except for C:N ratios (mol mol⁻¹).

	CN	CT	WS	MO
Cumulative DIN deposition (1850-2000)	11.5	11.6	6.9	6.9
Cumulative DIN input (1930-2000)	7.4	7.5	4.2	4.2
Cumulative ON input (1930-2000)	0.9	0.9	0.5	0.5
Cumulative DIN output (1930-2000)	3.5	2.4	2.0	2.7
Cumulative ON output (1930-2000)	1.3	1.5	0.7	0.7
In-lake retention of N (1930-2000) ¹⁾	1.7	1.1	0.4	0.4
Change in DIN content in lake water (1930-2000) ¹⁾	0.13	0.08	0.05	0.04
N retention in soil (1930-2000)	1.7	3.3	1.6	0.9
N content in soil (2000)	64.9	53.2	24.0	19.9
C content in soil (2000)	1429	1263	437	362
C:N in soil (2000)	22	24	18	18
Hypothetical C:N in soil (1930) ²⁾	23	25	20	19

¹⁾In-lake NO₃ reduction and change in DIN content in lake water (mol) were recalculated per total catchment area (mol m⁻²).

²⁾Hypothetical C:N ratio in soil in 1930 was estimated using the C:N ratio in 2000, C and N concentrations in soil in 2000 and N retention in soil over the 1930-2000 period (assuming negligible change in C content in soil during 1930 to 2000).

hypothetical decrease in C : N ratios of BF and TM soils fits well with conclusions made by Dise *et al.* (1998), which suggested that changes in soil C : N ratios may be a long-term process. The low soil C:N ratios (already in the 1930s) indicate a limited capacity of both mountain areas to assimilate elevated atmospheric deposition of DIN, even at the beginning of the mass budget period.

Response of forest and alpine ecosystems to DIN deposition

Estimated throughfall deposition of DIN was stable in BF during the 1880-1950 period (between 53 and 75 mmol m⁻² yr⁻¹) (Figs. 3 and 4). The average value of 67 mmol m⁻² yr⁻¹ (9.5 kg ha⁻¹ yr⁻¹) was close to the empirically derived threshold of 10 kg ha⁻¹ yr⁻¹ for European forest soils below which DIN leaching from soils was not expected to occur (e.g. Dise *et al.*, 1998; Curtis *et al.*, 1998). This outcome is supported by historical data from BF lakes where concentrations of NO₃ were < 2 µmol l⁻¹ in 1936 (Vesely and Majer, 1992), suggesting that nearly all DIN from throughfall deposition was removed by terrestrial and in-lake processes. Estimated DIN retention in soils, calculated on an annual basis from Eqn. (1), show that CN and CT catchments could assimilate high DIN deposition (50 and 60 mmol m⁻² yr⁻¹, respectively) during the 1930-1970 period. However, DIN retention in BF soils has declined in the last

two decades, varying between 0-60 mmol m⁻² yr⁻¹ in CT, and being close to zero or even negative (since the late 1980s) in CN catchment. Thus, soils in CN catchment have probably become a net source of DIN (practically all as NO₃) since the second half of the 1980s. The N_{out} : N_{in} ratios for the whole CN catchment-lake ecosystem has remained < 1 (Fig. 5) mainly because of the elevated in-lake retention of N which increases as a function of N loading (Kelly *et al.*, 1987).

Estimated bulk deposition of DIN varied between 35 and 45 mmol m⁻² yr⁻¹ (average of 41 mmol m⁻² yr⁻¹, i.e. ~6 kg ha⁻¹ yr⁻¹) in TM during the 1880-1950 period (Figs. 3 and 4). In 1937, Stangenberg (1938) found NO₃ concentrations between 0-4 µmol l⁻¹ in 16 TM lakes. This low DIN leaching suggested steady-state conditions within the catchment-lake ecosystem. As the in-lake retention of DIN was lower at that time, due to low DIN concentrations, most DIN input was probably retained in the soils. In the 1980-2000 period, estimated retention of DIN in alpine soils decreased to 10-20 mmol m⁻² yr⁻¹ in MO and WS catchments. In contrast, the ability of VW catchment to assimilate DIN was negligible and estimated DIN retention varied between -9 and 7 mmol m⁻² yr⁻¹ in the 1980-2000 period. Such results can be expected in VW catchment, where soil cover is sparse (Table 1). These sparse moraine soils with low C:N ratios (18) probably only adsorb and nitrify deposited NH₄ but

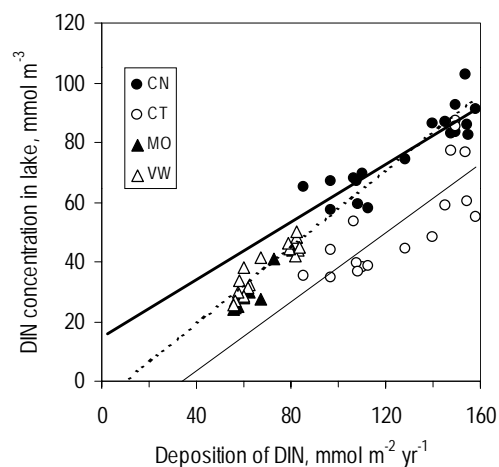


Fig. 6. Relationship between DIN deposition (throughfall for CN and CT and bulk for MO and VW lakes) and concentrations of DIN in the Bohemian Forest and Tatra lakes in the 1980-2000 period. Equations of linear regressions: CN, $y = 0.5x + 15$; CT, $y = 0.6x - 19$; MO, $y = 0.8x - 20$; VW, $y = 0.7x - 7$; $P < 0.001$ for all regressions. For lake codes see Table 1.

are not able to accumulate N. This fact may explain negligible NH_4 but high NO_3 concentrations (roughly equal to DIN concentration in precipitation), which were found in VW and some other TM lakes with rocky catchments (Kopáček *et al.*, 2000b).

The present DIN export from both BF and TM ecosystems fits well with the empirical models which link DIN leaching to current N deposition, soil pH or C : N ratios (Dise *et al.*, 1998; Gundersen *et al.*, 1998b), as well as to the ratios of DOC to dissolved DON in water (Harriman *et al.*, 1998). The decreasing trends in retention of DIN within both BF and TM soils suggest, however, that these dose-response functions may change over time. The historical change in composition of atmospheric deposition might partly contribute to the lower N retention within BF and TM ecosystems. Dise *et al.* (1998) have reported increasing N retention with increasing proportion of NH_4 in deposition. The NH_4 to NO_3 ratio in BF and TM bulk deposition is estimated to have decreased four-fold between the 1930s and 1990s (Figs. 3 and 4). Furthermore, increasing N deposition may induce changes in vegetation communities leading to changes in N leaching. Differences in vegetation status may also explain some inter-site variation in N export from BF and TM lakes (Kopáček *et al.*, 2001). None of these factors, however, can explain the different abilities of geographically adjacent catchments, CN and CT, to accumulate and export N (Table 5). Clearly, other mechanisms are affecting the ability of ecosystems to immobilise N, some of which may change during the period of elevated N deposition. An example of such changes has been observed in the mineralisation rate of soil organic

matter (Gundersen *et al.*, 1998a). In the BF lake catchments, Anderson *et al.* (2000) observed the highest rates of nitrification in the CN catchment. However, the reason is not clear and the processes involved require further study.

Despite these differences in the ability of catchments to retain N, DIN concentrations and transport from lakes generally decreased in parallel with decreasing deposition rate (Figs. 5 and 6). A similar pattern was observed in artificial manipulation experiments, when NO_3 leaching responded promptly to changes in N input (Gundersen *et al.*, 1998a). Consequently, N-saturation of BF and TM ecosystems seems to be reversible although the extent of change is difficult to predict. Linear regressions between DIN input and in-lake concentrations of DIN in the 1980-2000 period (Fig. 6) provide a rough estimate of critical levels of DIN deposition at which negligible concentrations of DIN were likely to leach. Critical DIN deposition of 32 and 25 $\text{mmol m}^{-2} \text{yr}^{-1}$ (i.e. $\sim 4 \text{ kg ha}^{-1}$) were estimated for CT and MO, respectively, which is $< 50\%$ of the steady-state DIN deposition in the 1930s. By comparison, the predominantly rocky catchment of VW with undeveloped moraine soils will only be able to assimilate a maximum 10 $\text{mmol m}^{-2} \text{yr}^{-1}$ of DIN deposition. The worst situation, in terms of ecosystem recovery from N-saturation, can be expected in CN which currently shows a net terrestrial loss of NO_3 . Even if DIN deposition falls to zero, DIN concentrations in CN would be $\sim 15 \mu\text{mol l}^{-1}$, although this may be an overestimate if steady-state is reached.

Conclusions

Negligible ecosystem outputs of S and DIN from BF and TM catchment-lake ecosystems in the 1930s suggested an equilibrium between deposition and retention. This equilibrium reflected relatively stable S and DIN emissions over previous decades. Then, the rapid increases of S and DIN deposition resulted in pronounced changes in the chemistry of both terrestrial and aquatic parts of these ecosystems. Sulphur accumulation in soils partly mitigated the increase in lake water SO_4 during the 1930–1990 period, however, soil desorption has recently become an important source of SO_4 for surface waters in both BF and TM after the respective 80% and 50% decline in S deposition. The new steady-state conditions in S dose and export will be reached sooner in the alpine than in forest ecosystems due to the lower amount of S accumulated in soils.

Lake water concentrations of NO_3 generally followed the increasing, as well as decreasing, DIN deposition trends in both areas. Nitrogen saturation of these ecosystems seems to reflect DIN dose and is largely reversible despite the complexity of the N-biogeochemical cycle. The ability of

terrestrial ecosystems to assimilate DIN deposition, however, declined between 1930 and 2000 (CT, WS, and MO) and/or completely changed from N retention to N production (CN).

Using the status of BF and TM lakes in the 1930s as a measure of “unaffected” Central European mountainous ecosystems, the threshold levels of S and N emissions, which should be reached to enable recovery from acidification and N-saturation can be estimated. The present Central European emission rates of S have nearly declined to the required threshold level ($< 60 \text{ mmol m}^{-2} \text{ yr}^{-1}$) and future soil and water acidification due to SO_4 leaching will result primarily from leaching of S accumulated in soils. To reach the DIN deposition of the 1930s, the recent Central European emissions of DIN should be reduced to $< 80 \text{ mmol m}^{-2} \text{ yr}^{-1}$. Even such a large reduction, however, will probably not be sufficient for the complete recovery of the ecosystems from N-saturation due to changes in their ability to retain N.

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Appendix 1

Trends in emissions of sulphur and nitrogen compounds

The historical Czech and Slovak (CS) emission trends for SO_2 and NO_x were reconstructed using data from Yearbooks of the Czech and Slovak Statistical Offices for the 1980–1999 period and calculated data (1850–1980 period). Anthropogenic emissions of SO_2 were calculated according to Várhelyi (1985) on the basis of fuel consumption (burning of brown and hard coal, oil, and wood). Historical trends in the average S content of coal and S retention in ash were obtained from Mylona (1993). Production of SO_2 from

smelting of sulphidic ores, which was an important source of S emission in the Czech Republic and Slovakia before 1900, was estimated by Holub (pers. comm.). When compared to the statistical yearbook data, the calculated data on anthropogenic SO_2 emissions were on average 8% higher in the 1980–1990 period. Emissions of SO_2 from natural sources were assumed to be $9 \text{ mmol m}^{-2} \text{ yr}^{-1}$ (non-sea salt S deposition in remote continental areas; Galloway *et al.*, 1985) throughout the 1850–2000 period.

Anthropogenic emissions of NO_x were calculated according to Pacyna *et al.* (1991) on the basis of fuel consumption (lignite and hard coal, oil, gas, and wood) in stable and mobile sources. Emissions of NO_x from natural sources (soil processes, burning of straw and stubble) in Europe were estimated as 3% of anthropogenic emission in the 1980s (Pacyna *et al.*, 1991). Applying this approach, the natural NO_x production in the Czech Republic and Slovakia was estimated as $\sim 5 \text{ mmol m}^{-2} \text{ yr}^{-1}$ and was assumed to be constant throughout the 1850–2000 period. The difference between the calculated total emission rate of NO_x and statistical yearbook data varied from –6% to 6% in the 1980–1990 period.

The historical Czech and Slovak emission trends for NH_3 were calculated for the whole 1850–2000 period according to Asman *et al.* (1988) from data on livestock production (cattle, pigs, sheep, goats, horses and poultry) and nitrogenous fertiliser production and consumption. Emissions of NH_3 from natural sources ($\sim 9 \text{ mmol m}^{-2} \text{ yr}^{-1}$) was roughly estimated according to Buijsman *et al.* (1987) as $\sim 12\%$ of anthropogenic emissions in Europe in the 1980s and was assumed to be constant throughout the 1850–2000 period. The difference between the calculated total emission rate of NH_3 and statistical yearbooks data varied from –14% to 3% in the 1985–1999 period, with the average of –5%.

Data on Central European (Germany, Poland, Czech Republic, and Slovakia) emissions of SO_2 , NO_x , and NH_3 after 1980 came from Berge (1997) and Yearbooks of the National Statistical Offices. The historical trend for Central European emissions of SO_2 before 1980 came from Mylona (1993).

Appendix 2

Estimated trends in deposition of sulphur and nitrogen compounds

Data on atmospheric deposition of SO_4 , NO_3 , and NH_4 came from the following sources: (1) Wet-only deposition in the Czech Republic (CR), based on data from stations

Svratouch, Košetice, and Hradec Králové (Mackù *et al.*, 1959, and the Czech Hydrometeorological Institute, 1978–2000 period). (2) Bulk deposition in northern Slovakia (NS) from the Chopok station, situated at 2008 m a.s.l. $\sim 40 \text{ km}$ south-west of TM (Mackù *et al.*, 1959, and the Slovak Hydrometeorological Institute, 1978–1999 period). (3) Atmospheric deposition in BF in the 1992–2000 period, based on one bulk and two throughfall sites differing in altitude (Hruška *et al.*, 2000). (4) Bulk deposition in TM, measured at Starolesnianske Lake (southern part; 2000 m a.s.l.) in the 1997–1999 period (Stuchlík, unpubl. data) and at Hala Gasienicowa (northern part; 1520 m a.s.l.) in the 1993–1998 period (Lydersen *et al.*, 1997, The MOLAR Chemistry Group, 1999).

Relationships used for estimation of SO_4 , NH_4 , and NO_3 deposition in CR (wet-only) and NS (bulk) from the respective CS emissions of SO_2 , NH_3 and NO_x were as follows: (1) SO_4 in CR: linear regression between measured SO_4 deposition in CR and CS emissions of SO_2 ($P < 0.001$). (2) NH_4 in CR: linear regression between measured NH_4 deposition in CR and CS emissions of NH_3 ($P < 0.001$). (3) NO_3 in CR: ratio of 0.21 ± 0.03 (average \pm standard deviation) between measured deposition of NO_3 in CR and CS emissions of NO_x . (4) SO_4 in NS: linear regression between measured SO_4 deposition at Chopok and CS emissions of SO_2 ($P < 0.01$). (5) NH_4 in NS: linear regression between measured NH_4 deposition at Chopok and CS emissions of NH_3 ($P < 0.01$). (6) NO_3 in NS: ratio of 0.23 ± 0.08 between measured deposition of NO_3 at Chopok and CS emissions of NO_x .

Estimation of SO_4 , NH_4 and NO_3 deposition in the Bohemian Forest (BF) and Tatra Mountains (TM) were based on estimated trends in their deposition in CR and NS, respectively, using the following ratios: (1) Measured throughfall deposition in BF to measured wet-only deposition in CR: SO_4 , 4.5 ± 0.8 and 1.6 ± 0.4 for the period of CS emission higher and lower than $100 \text{ mmol m}^{-2} \text{ yr}^{-2}$, respectively; NH_4 , 1.4 ± 0.3 ; and NO_3 , 2.7 ± 0.5 . (2) Measured bulk deposition in BF to measured wet-only deposition in CR: SO_4 , 1.2 ± 0.3 ; NH_4 , 1.2 ± 0.3 ; and NO_3 , 1.6 ± 0.2 . (3) Measured bulk deposition in TM to measured bulk deposition in NS (Chopok): SO_4 , 0.9 ± 0.3 ; NH_4 , 0.7 ± 0.1 ; and NO_3 , 0.8 ± 0.2 . The ratios were calculated for all available paired data and arithmetic means were used in the above calculations. Uncertainty associated with the deposition estimates was estimated as coefficient of variation of the mean, i.e. $< \pm 30\%$.

